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⑰ Composition and method for cleaning hydrocarbon oil from hard surfaces.

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Description

The present invention relates to methods of cleaning oil/rock mixtures in oil drilling operations and especially to cleaning of drilling oil from rock cuttings on offshore drilling rigs, removal of oil from the face of newly drilled holes prior to reinforcement with casing, and to the cleaning of oil muds from drilling rigs.

In the process of drilling for oil and gas, it is necessary for a number of reasons, to use a drilling fluid or drilling mud. The types of drilling fluid or mud in common use are:—

- a) water based.
- b) oil based.
- 10 c) water in oil emulsion based (invert).

Oil based drilling media (b) may also contain water in the form of water in oil emulsion. It is customary in the art to refer to a drilling medium containing up to about 15% aqueous phase by volume as oil based. Those drilling media referred to as invert fluids or muds, (c) generally contain between 15% and 55% water. This patent application is particularly concerned with types (b and c) both of which are included in the term "oil" as used herein, together with crude and refined mineral oils.

One of the functions of drilling fluid is to carry drill cuttings from the drill bit to the surface, the cuttings are then removed by physical techniques, for example, by using shale shakers, screens, cyclones, and centrifuges. After removal of the cuttings the drilling fluid is re-used and the cuttings are disposed of. If the drilling is offshore then the cuttings are disposed of into the sea, where in the case of aqueous drilling fluids the cuttings disperse and settle without causing significant problems. However, in the case of oil drilling fluids the cuttings are oil wet and settle rapidly to the sea bed below the drilling rig and form an oily, sticky mass, which can interfere with drilling operations, for example, by hindering the movement of divers involved in sub-sea construction and maintenance work. It is thought that the swelling of clays in the cuttings is responsible for the formation of this mass. In addition, the cuttings cause oil pollution through gradual release of the oil.

One technique to remove oil from cuttings is to wash the cuttings with a solvent such as diesel, this has the effect of removing most of the oil but still leaves the surfaces contaminated with hydrocarbons, which can gradually be released to the environment. Another way is to use a water miscible solvent, such as a glycol ether, but these are expensive. Yet another way is to wash the cuttings in sea water using good agitation to dislodge the oil from the surface of the cuttings. This process can be used either as the sole process for removing the drilling oil from the cuttings, or as a second step to remove an oil solvent from cuttings previously washed with a hydrocarbon. This process can be improved by adding a surfactant to the sea water, to lower the oil/water interfacial tension. The cuttings may then be discharged to the sea where they disperse and settle over a wide area of sea bed rather than accumulate directly in the area of the drilling operations. The oil in water emulsion which is formed as a result of washing the cuttings may be discharged to the sea where fine dispersion of the oil will facilitate its breakdown by micro-organisms.

A commonly used surfactant for the foregoing purposes is a C₈₋₁₁ alcohol six mole ethoxylate. A variety of alkoxyated non-ionic surfactants are known in the detergent art which are sometimes used as ingredients of detergent or shampoo formulations for various purposes, usually in admixture with anionic or cationic surfactants.

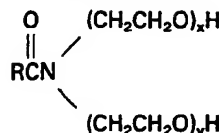
Another category of known surfactant comprises the alkyl alkanolamides. These are not normally used as cleaning agents in their own right, but are widely used as minor ingredients of detergent and shampoo formulations to promote foaming.

Examples of prior art referring to the use of polyalkoxyated non-ionics surfactants and/or of alkyl alkanolamides as ingredients of various types of cleaning composition, or other products, include EP—A—0018630, AT—B—179693, DE—A—1621447, EP—A—0034393, GB—A—717866, US—A—2831814, US—A—4233174, FR—A—1413197, US—A—3031409, US—A—3507806, US—A—4002579, US—A—4102825, US—A—3823094, US—A—4097306, US—A—4012341, US—A—4118404 and US—A—4233174. An object of the present invention is to provide more effective methods of cleaning oil from rock cuttings.

50 An object of the present invention is to provide more effective methods of cleaning oil from rock cuttings. A further object of our invention is to provide a method whereby oil can be separated from the emulsion resulting from cleaning of the cuttings.

We have discovered that a particular blend of an ethoxylated nonionic surfactant with an alkanolamide exhibits a synergistic effect permitting the more efficient cleaning of oil from rock cuttings. We have further discovered according to a preferred embodiment of our invention that when the emulsions of oil in water formed by cleaning according to our invention are heated, the emulsion is readily broken and the oil may then be recovered.

Accordingly, our invention provides a method of removing oil from solid surfaces which comprises contacting the surfaces with an aqueous solution containing at least 0.5% by weight of a mixture of (A) from 5 to 95% by weight of at least one alkoxyated alcohol, carboxylic acid, alkylphenol, or nonionic phosphate ester, having in each case at least one alkyl group with from 6 to 22 carbon atoms and from 1 to 20 ethyleneoxy groups, with (B) from 95 to 5% by weight of at least one alkanolamide of the formula:—



wherein R is an alkyl group, having from 5 to 17 carbon atoms and x and y are each chosen from 0 and integers from 1 to 12, such that the average value of (x+y) is from 1 to 12.

Preferably (A) is primary straight or branched chain alcohol having from 6 to 18 carbon atoms and alkoxyated with from 1 to 10 ethylene-oxy groups.

(A) may alternatively be normal or branched chain alkanolic or alkenoic acid having from 7 to 23 e.g. 8 to 20 carbon atoms, alkoxyated with from 1 to 10 ethylene-oxy groups; straight or branched chain alkyl phenol with from 6 to 12 aliphatic carbon atoms, alkoxyated with from 1 to 12 ethylene-oxy groups; nonionic phosphoric acid ester having at least one straight or branched chain alkyl group with from 6 to 22 carbon atoms, at least one alkoxy or polyalkoxy group with from 1 to 20 ethylene-oxy units.

(B) typically has from 1 to 4 ethyleneoxy groups. While we have discovered that monoethanolamides are particularly effective synergists, and may be preferred for use in warm climates, concentrated mixture of monoethanolamide with component (A) tend to be insufficiently fluid at low temperatures for convenient handling under the conditions which may be encountered in, for example, North Sea operations. For such low temperatures we prefer to use diethanolamides.

Typically, a mixture of (A) and (B) is supplied as a concentrate which is dissolved in, or diluted with, water to provide the cleansing solution at the site of the rig. Such concentrates optionally contain a solvent such as water or a water miscible alcohol, glycol or glycol ether, e.g. isopropanol, ethylene glycol, propylene glycol, polyethylene glycol, or any other mono-, di- or trihydroxy alcohol, or alcohol ether, having from 2 to 8 carbon atoms, as required to provide a fluid, pourable composition under the conditions likely to be encountered. The concentrate may, additionally, contain minor proportions of hydrotropes, such as alkaline earth, sodium or potassium mono- di- or tri-alkyl benzene sulphonate salts having less than six aliphatic carbon atoms, e.g. toluene or xylene sulphonates, phosphate esters salts, preservatives, such as formalin, dyes and/or perfumes. Water may be present in any convenient proportion between zero and the final working concentration of the cleaner. Generally, the lower the proportion of the water the greater the convenience for transport and storage of the concentrate. These considerations however must be balanced against the preference for a stable, pourable composition. Organic solvents can add appreciably to the cost of the composition and are preferably, therefore used sparingly e.g. less than 50% and preferably less than 20% of the weight of the concentrate.

The concentrate may typically contain from 5 to 95% by weight of (A) and from 95 to 5% by weight of (B). Preferably however (A) is present in concentrations greater than 10% by weight, most preferably greater than 20% and usually greater than 30%. (B) is also preferably present in concentrations of greater than 10% by weight, more preferably greater than 20% and usually greater than 30%. We generally prefer that each of A and B should be present in proportions of greater than 20% by weight, e.g. 20-60% together, optionally with up to 10% water and up to 10% of water miscible, hydroxyl containing solvent. A suitable mixture contains from 40% to 60% of (A), from 60% to 40% of (B) and from 0 to 20% of solvent.

The concentrate is dissolved or dispersed in water at the site of application. When used at offshore locations, the concentrate may conveniently be dissolved or dispersed in sea water. Typically, the concentrate is diluted to from 0.5% to 10% active matter by weight preferably from 1 to 6. We do not exclude higher concentrations, but they are unlikely to prove cost effective. The component (A) in our concentrate may conveniently be an ethoxylated alcohol having from 8 to 14 carbon atoms and from 2 to 7 ethylene oxide groups.

When used to clean rock cuttings, the cuttings are preferably agitated with the solution of the concentrate in water or brine, for a sufficient time to emulsify a substantial proportion of the oil. The emulsion may then be separated from the cuttings which, when sufficiently clean, are dumped. The emulsion may be discharged. However, according to a preferred embodiment of our invention the oil is recovered from the emulsion by moderate heating. Typically temperatures in excess of 40°C e.g. 50 to 70°C are sufficient to break the emulsion and permit recovery of the separated oil phase.

The cleaning solution according to our invention may also be injected into bore holes to clean oil from the sides of the rock. This is necessary when a casing is to be bonded with cement to the sides of the bore hole. The solution may also be used according to our invention to clean oil mud from the rigs themselves and generally to remove viscous hydrocarbon oils from hard surfaces.

The solution will be illustrated by the following examples:

The products were tested as follows:

Cuttings wash test method

a) 43 grams of oil mud cuttings obtained from a North Sea drilling operation were added to 150 g of X% active matter surfactant solution in synthetic sea water.

b) This was stirred for 5 minutes using a "Janke & Kunkel" (Trade Mark) stirrer at setting 2 at 800 rpm.

c) The mixture was allowed to stand for five minutes after which time the liquid was decanted. This liquid contained the emulsified oil which could be separated by warming to above 40°C.

d) The mixture was then made up to 150 ml with standard sea water and stirred for a further minute as in b).

5 e) The mixture was then filtered through two layers of muslin.

f) 20 g of washed cuttings were weighed accurately (W1) into a 250 ml round bottomed flask and the water content was determined by the Dean and Stark method using 100—120 petroleum ether. The weight of water removed was determined as W2.

10 g) A further 10 g of the washed cuttings were accurately weighed (W3) into an evaporating dish and dried to constant weight (W4) at 110°C.

The weight of oil on the cuttings,

$$W5 = W3 - W4 - \frac{W2 \times W3}{W1}$$

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The weight of oil left on the cuttings expressed as a percentage of weight of dry cuttings+weight of oil

$$W0 = \frac{W5}{W4 + W5} \times 100$$

20

The test was performed in duplicate. It should be noted that we have found that the amount of oil removed from the surface of cuttings by any given surfactant or blend of surfactants is dependent on the age of the cuttings, more oil being removed from fresh cuttings than from aged cuttings.

25

Example 1

Using the test method above, the following results were obtained using oil mud cuttings from the North Sea.

30

Surfactant	% Oil remaining on cuttings
None	virtually 100%
A (5%)	6.4%
B (5%)	7.1%
A (2.5%)+B (2.5%)	3.9%

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40

A=C9/C11 primary alcohol nominal 6 mole ethoxylate.
B=coconut monoethanolamide+2 mole ethylene oxide.

Example 2

45

Surfactant	% Oil remaining on cuttings
A (5%)	1.2%
B (5%)	3.5%
A (2.5%)+B (2.5%)	0.5%

50

A=C10/C12 primary alcohol nominal 5 mole ethoxylate.
B=coconut diethanolamide.

55

Example 3

Surfactant	% Oil remaining on cuttings
A (5%)	4.4%
B (5%)	3.5%
A (3.75%)+B (1.25%)	2.8%

60

65

A=C8/C10 primary alcohol nominal 4 mole ethoxylate.
B=coconut diethanolamide.

Example 4

	Surfactant	% Oil remaining on cuttings
5	A (5%)	4.1%
	B (5%)	3.5%
	A (1.25%)+B (3.75%)	2.3%

10 A=nonyl phenol nominal 9 mole ethoxylate.
B=coconut diethanolamide.

In addition the emulsion decanted in step c) and obtained using A (1.5%)+B (3.75%) was heated to 40°C and separated into distinct oil and aqueous phases.

Example 5

	Surfactant	% Oil remaining on cuttings
20	A (5%)	14.4%
	B (5%)	3.5%
	A (1.25%)+B (3.75%)	3.3%

25 A=oleic acid nominal 8 mole ethoxylate.
B=coconut diethanolamide.

Example 6

	Surfactant	% Oil remaining on cuttings
30	A (5%)	7.5%
	B (5%)	3.5%
35	A (3.75%)+B (1.25%)	2.6%

A=mixture of mono and di- C8/C10 alkyl phosphate nominal 5.4 mole ethoxylate.
B=coconut diethanolamide.

40 The emulsion decanted in step c) and obtained using A (3.75%)+B (1.25%) was heated to 40°C and separated into distinct oil and aqueous phases.

Example 7

45 A concentrate was prepared for use according to the invention consisting of 45% by weight of C10/C12 fatty alcohol 5 mole ethoxylate, 45% by weight coconut diethanolamide, 5% by weight propylene glycol, 5% by weight water. The product was fluid and stable at temperatures between -5°C and 35°C and readily dispersed in sea water. When evaluated in the above cuttings cleaning test the results were as follows.

		% Oil remaining on cuttings
50	A (5% AM)	4.3%
	Formulation of Example 7 (5% AM)	0.5%

55 A=C9/C11 primary alcohol nominal 6 mole ethoxylate. This is the surfactant most commonly used for cleaning oil mud cuttings.

The emulsion decanted in step c) of the method and obtained using the formulation of Example 7, was heated to 50°C and separated into distinct oil and aqueous phases.

Example 8

The following test was used to show the effectiveness of the blend of nonionic surfactants of types A and B as defined above, for removing oil from metal surfaces.

65 a) A mild steel plate was washed thoroughly in household detergent solution followed by rinsing under the tap and then with acetone.

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b) One surface of the plate was coated evenly with 0.4 g of hydrocarbon oil, e.g. crude oil.
c) 0.6 g of test solution was then mixed intimately with the surface oil, and the plate was allowed to rest horizontally with the coated face uppermost for 15 minutes.

d) The surface was then washed with 200 cm³ of synthetic sea water from a laboratory wash bottle.
e) The amount of oil remaining on the plate was assessed visually.

In this test, the test solution used contained 7.5% of a C10/C12 fatty alcohol 5 mole ethoxylate, 7.5% coconut diethanolamide and 85% water. The oil was substantially removed from the surface of the mild steel leaving a clean non-oily surface.

In a further test, the test solution was a commercial hydrocarbon solvent based degreaser believed to contain emulsifiers. The mild steel was less thoroughly cleaned and the surface was oily.

Example 9

The test method described above (examples 1—7) was used, but the concentration of surfactant was changed.

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Wt.% of surfactant	% Oil remaining on cuttings	
	A (Comparative)	Formulation of Example 7
1	14.0	13.1
3	5.9	2.2
5	4.3	0.5
7	3.7	0.5
10	3.7	0.5

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A=C9/C11 primary alcohol nominal 6 mole ethoxylate.

This is the surfactant most commonly used for cleaning oil mud cuttings and over the wide concentration range studied was clearly less effective.

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Alkyl distribution of alcohols used in the Examples

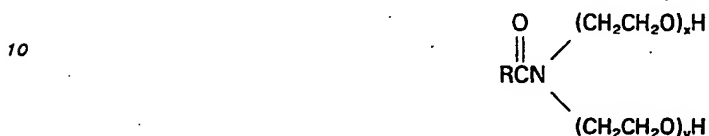
The following are typical distributions.

Carbon No.	Example			
	1 & 7	2, 7 & 8	3	6
6	—	—	3.5%	3.5%
7	—	—	—	—
8	1.7%	—	69.5%	69.5%
9	20.1%	—	—	—
10	39.2%	85.0%	24.5%	24.5%
11	28.3%	—	—	—
12	4.1%	8.5%	2.5%	2.5%
13	—	—	—	—
14	—	6.2%	—	—
15	—	—	—	—
16	—	0.3%	—	—

In Example 7, surfactant A is the same as A in Example 1.

Claims

1. A method for the removal of oil from solid surfaces which comprises contacting the surfaces with an aqueous solution containing at least 0.5% by weight of a mixture of (A) from 5 to 95% by weight of at least one alkoxyated alcohol, carboxylic acid, alkyl phenol, or nonionic phosphate ester, having in each case an alkyl or alkenyl group with from 6 to 22 carbon atoms and from 1 to 20 ethylene oxide groups with (b) from 95 to 5% by wt. of at least one ethylolamide of the formula



- wherein R is an alkyl group having from 5 to 17 carbon atoms and x and y are each chosen from 0 and integers from 1 to 12, such that the average value of (x+y) is from 1 to 12.
2. A method according to claim 1 wherein (A) is a primary, straight or branched chain alcohol having from 6 to 18 carbon atoms ethoxylated with from 1 to 10 ethylene oxide groups.
3. A method according to claim 1 wherein (A) is a normal or branched chain alkanolic or alkenolic acid having from 8 to 20 carbon atoms alkoxyated with from 1 to 10 ethyleneoxy groups.
4. A method according to claim 1 wherein (A) is a straight or branched chain alkyl phenol having from 6 to 12 aliphatic carbon atoms alkoxyated with from 1 to 12 ethylene oxide groups.
5. A method according to claim 1 wherein (A) is a nonionic phosphoric acid ester having at least one straight or branched chain alkyl group having from 6 to 22 carbon atoms and at least one ethylene group or polyalkoxy group having up to 20 ethyleneoxy units.
6. A method according to any foregoing claims wherein (B) has from 1 to 4 ethyleneoxy groups.
7. A method according to claim 6 wherein (B) is an alkyl monoethanolamide.
8. A method according to claim 6 wherein (B) is an alkyl diethanolamide.
9. A method according to any foregoing claim wherein (A) and (B) are each present in a proportion of more than 20% of the total active weight of the mixture.
10. A method according to any foregoing claim wherein the aqueous solution is sea water.
11. A method according to any foregoing claim wherein the mixture is present in the aqueous solution in a concentration of from 0.5% to 10%.
12. A method according to any foregoing claim for washing oil rig cuttings.
13. A method according to any foregoing claims for washing structures.
14. A method according to claim 13 for cleaning surfaces of oil rigs.
15. A method according to any foregoing claim wherein the aqueous solution is recovered after washing and heated sufficiently to effect separation of any oil emulsified therein.
16. A concentrate for use in the preparation of aqueous solutions for use according to the method of any foregoing claim, consisting essentially of from 20% to 60% by wt. of (A), from 20% to 60% by wt. of (B), up to 10% by wt. of water and up to 10% by wt. of a water miscible, hydroxyl containing organic solvent.
17. A concentrate according to claim 16 wherein (a) is an ethoxylated alcohol having from 8 to 14 carbon atoms and from 2 to 7 ethyleneoxy groups.
18. A concentrate according to either of claims 16 and 17 wherein (b) is an alkyl diethanolamide.
19. A concentrate according to any of claims 16 to 18 wherein the solvent is a water miscible mono di- or tri-hydroxy alcohol or alcohol ether having from 2 to 8 carbon atoms.
20. Aqueous solutions for use in the method of any of claims 1 to 15 formed by dilution of a concentrate according to any of claims 16 to 19 with water, and containing at least 0.5% surface active matter.
21. Sea water for use in the method of any of claims 1 to 15 having dissolved therein a concentrate according to any of claims 16 to 19 and containing at least 0.5% surface active matter.

Patentansprüche

1. Verfahren zur Entfernung von Kohlenwasserstoff-Öl von festen Oberflächen, dadurch gekennzeichnet, daß man die Oberflächen mit einer wäßrigen Lösung, die wenigstens 0,5 Gewichts-% eines Gemisches aus (A) 5 bis 95 Gew.-% wenigstens eines alkoxylierten Alkohols, einer Carbonsäure, eines Alkylphenols oder eines nicht-ionischen Phosphatesters, wobei diese in jedem Fall eine Alkyl- oder Alkenyl-Gruppe mit 6 bis 22 Kohlenstoffatomen und 1 bis 20 Ethylenoxidgruppen aufweisen, mit (B) 95 bis 5 Gew.-% wenigstens eines Ethylolamides der Formel



in der R eine Alkylgruppe mit 5 bis 17 Kohlenstoffatomen darstellt und x und y jeweils ausgewählt sind aus 0 und den ganzen Zahlen von 1 bis 12 derart, daß der Durchschnittswert von (x und y) 1 bis 12 beträgt, in Kontakt bringt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß (A) ein primärer gradkettiger oder verzweigter Alkohol mit 6 bis 18 Kohlenstoffatomen, der mit 1 bis 10 Ethylenoxidgruppen ethoxiliert ist, ist.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß (A) eine normale oder verzweigtkettige Alkan- oder Alkencarbonsäure mit 8 bis 20 Kohlenstoffatomen, die mit 1 bis 10 Ethylenoxygruppen alkoxyliert ist, darstellt.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß (A) ein gradkettiges oder verzweigtes Alkylphenol mit 6 bis 12 aliphatischen Kohlenstoffatomen, das mit 1 bis 12 Ethylenoxygruppen alkoxyliert ist, darstellt.

5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß (A) ein nicht-ionischer Phosphorsäureester mit wenigstens einer gradkettigen oder verzweigten Alkylgruppe mit 6 bis 22 Kohlenstoffatomen und wenigstens einer Ethylenoxygruppe oder Polyalkoxygruppe mit bis zu 20 Ethylenoxy-Einheiten darstellt.

6. Verfahren nach den vorhergehenden Ansprüchen, dadurch gekennzeichnet, daß (B) 1 bis 4 Ethylenoxygruppen aufweist.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß (B) ein Alkylmonoethanolamid ist.

8. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß (B) ein Alkyldiethanolamid ist.

9. Verfahren nach den vorhergehenden Ansprüchen, dadurch gekennzeichnet, daß (A) und (B) jeweils in einem Mengenverhältnis von mehr als 22% des gesamten aktiven Gewichts des Gemisches vorhanden sind.

10. Verfahren nach den vorhergehenden Ansprüchen, dadurch gekennzeichnet, daß die wäßrige Lösung Meerwasser ist.

11. Verfahren nach den vorhergehenden Ansprüchen, dadurch gekennzeichnet, daß das Gemisch der wäßrigen Lösung in einer Konzentration von 0,5% bis 10% vorliegt.

12. Verfahren nach den vorhergehenden Ansprüchen zum Abwaschen von Bohrkernmaterial aus Ölbohrungen.

13. Verfahren nach den vorhergehenden Ansprüchen, zum Abwaschen von Bauten.

14. Verfahren nach Anspruch 13 zum Reinigen von Oberflächen von Ölbohrgeräten.

15. Verfahren nach den vorhergehenden Ansprüchen, dadurch gekennzeichnet, daß die wäßrige Lösung nach dem Waschen gewonnen und ausreichend hoch erhitzt wird, bis das darin emulgierte Öl daraus abgetrennt wird.

16. Konzentrat für die Verwendung bei der Herstellung wäßriger Lösungen zur Anwendung gemäß dem Verfahren nach den vorhergehenden Ansprüchen, hauptsächlich bestehend aus 20 bis 60 Gew.-% (A), 20 bis 60 Gew.-% (B), bis zu 10 Gew.-% Wasser und bis zu 10 Gew.-% eines mit Wasser mischbaren, Hydroxylgruppen enthaltenden organischen Lösungsmittels.

17. Konzentrat nach Anspruch 16, dadurch gekennzeichnet, daß (A) ein ethoxylierter Alkohol mit 8 bis 14 Kohlenstoffatomen und 2 bis 7 Ethylenoxygruppen ist.

18. Konzentrat nach den Ansprüchen 16 und 17, dadurch gekennzeichnet, daß (B) ein Alkyldiethanolamid ist.

19. Konzentrat nach den Ansprüchen 16 bis 18, dadurch gekennzeichnet, daß das Lösungsmittel ein mit Wasser mischbarer Mono-Di- oder Tri-Hydroxy-Alkohol oder Alkohol-Äther mit 2 bis 8 Kohlenstoffatomen ist.

20. Wäßrige Lösungen zur Verwendung bei den Verfahren nach den Ansprüchen 1 bis 15, gebildet durch Verdünnung eines Konzentrats nach den Ansprüchen 16 bis 19 mit Wasser und enthaltend wenigstens 0,5% oberflächenaktive Substanz.

21. Meerwasser zur Verwendung bei den Verfahren nach den Ansprüchen 1 bis 15 mit darin gelöstem Konzentrat nach den Ansprüchen 16 bis 19 und enthaltend wenigstens 0,5% oberflächenaktive Substanz.

50 Revendications

1. Un procédé pour l'élimination d'une huile des surfaces solides, caractérisé en ce que l'on met les surfaces en contact avec une solution aqueuse contenant au moins 0,5% en poids d'un mélange (A) de 5 à 95% en poids d'au moins un alcool, un acide carboxylique, un alkylphénol ou un ester phosphorique non ionique alcoylé, comportant dans chaque cas un groupe alkyle ou alcényle avec 6 à 22 atomes de carbone et 1 à 20 groupes oxyde d'éthylène, avec (B) 95 à 5% en poids d'au moins un éthylolamide de formule:



dans laquelle R est un groupe alkyle ayant 5 à 17 atomes de carbone et x et y sont choisis chacun parmi 0 et les nombres entiers de 1 à 12 de façon que la valeur moyenne (x+y) se situe entre 1 et 12.

2. Un procédé selon la revendication 1, dans lequel (A) est un alcool primaire à chaîne droite ou ramifiée ayant 6 à 18 atomes de carbone, éthoxylé avec 1 à 10 groupes oxyde d'éthylène.
3. Un procédé selon la revendication 1, dans lequel (A) est un acide alcanolique ou alcenoïque à chaîne normale ou ramifiée possédant 8 à 20 atomes de carbone, alcoylé avec 1 à 10 groupes oxyde d'éthylène.
- 5 4. Un procédé selon la revendication 1, dans lequel (A) est un alkylphénol à chaîne droite ou ramifiée possédant 6 à 12 atomes de carbone aliphatique, alcoylé avec 1 à 12 groupes oxyde d'éthylène.
5. Un procédé selon la revendication 1, dans lequel (A) est un ester d'acide phosphorique non ionique comportant au moins un groupe alkyle à chaîne droite ou ramifiée de 6 à 22 atomes de carbone et au moins un groupe alcoxy ou un groupe polyalcoxy possédant jusqu'à 20 unités d'oxyde d'éthylène.
- 10 6. Un procédé selon l'une quelconque des revendications précédentes, dans lequel (B) comporte 1 à 4 groupes oxyde d'éthylène.
7. Un procédé selon la revendication 6, dans lequel (B) est un alkyl monoéthanolamide.
8. Un procédé selon la revendication 6, dans lequel (B) est un alkyl diéthanolamide.
9. Un procédé selon l'une quelconque des revendications précédentes, dans lequel (A) et (B) sont
- 15 présents chacun dans une proportion supérieure à 20% en poids actif total du mélange.
10. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la solution aqueuse est de l'eau de mer.
11. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange est présent dans la solution aqueuse à une concentration de 0,5% à 10%.
- 20 12. Un procédé selon l'une quelconque des revendications précédentes, destiné au lavage des débris des installations de forage du pétrole.
13. Un procédé selon l'une quelconque des revendications précédentes, destiné au lavage des structures.
14. Un procédé selon la revendication 13, destiné au nettoyage des surfaces des installations de forage.
- 25 15. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la solution aqueuse est récupérée après lavage et est suffisamment chauffée pour provoquer une séparation de l'huile qui y est émulsionnée.
16. Un concentré destiné à la préparation de solutions aqueuses pour utilisation selon le procédé de l'une quelconque des revendications précédentes, comportant essentiellement 20% à 60% en poids de (A),
- 30 20% à 60% en poids de (B), jusqu'à 10% en poids d'eau et jusqu'à 10% en poids d'un solvant organique hydroxylé miscible à l'eau.
17. Un concentré selon la revendication 16, dans lequel (A) est un alcool éthoxylé possédant 8 à 14 atomes de carbone et 2 à 7 groupes oxyde d'éthylène.
18. Un concentré selon l'une ou l'autre des revendications 16 et 17, dans lequel (B) est un alkyl
- 35 diéthanolamide.
19. Un concentré selon l'une quelconque des revendications 16 à 18, dans lequel le solvant est un mono-, di- ou trialcool miscible à l'eau ou un alcool éther comptant 2 à 8 atomes de carbone.
20. Solutions aqueuses destinées au procédé de l'une quelconque des revendications 1 à 15, obtenues par dilution d'un concentré selon l'une des revendications 16 à 19 avec de l'eau et qu'elles contiennent au
- 40 moins 0,5% de matière tensioactive.
21. Eau de mer destinée au procédé de l'une quelconque des revendications 1 à 15, ayant dissous un concentré selon l'une quelconque des revendications 16 à 19 et quelle contient au moins 0,5% de matière tensio-active.

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